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MANUFACTURE OF AROMATIC CARBONIC ACID ESTERS

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[There are no amendments to this patent.]

Abstract

Objective

To offer a method for the efficient manufacture of aromatic carbonic acid esters while decreasing the amount of by-product.

Means to solve

A method for manufacturing aromatic carbonic acid esters, wherein an aromatic hydroxy compound is allowed to react with

oxygen and carbon monoxide, where said reaction is carried out in the presence of an aromatic nitro compound.

Claims

1. A method for manufacturing aromatic carbonic acid esters, wherein an aromatic hydroxy compound is allowed to react with oxygen and carbon monoxide, characterized in that said reaction is carried out in the presence of an aromatic nitro compound.

2. The method according to Claim 1, wherein the aforementioned reaction is carried out in the presence of palladium system catalyst.

3. The method according to Claim 2, wherein the aforementioned palladium system catalyst is a catalyst that comprises (A) one or more types of substances selected from palladium and palladium compounds, (B) one or more types of substances selected from among metal or metal compounds having an oxidation potential that is greater than that of palladium, and (C) one or more types of substances selected from among halides.

4. The method according to Claim 3, wherein (A) above is palladium acetate or palladium/carbon.

5. The method according to Claim 3, wherein (B) above is a lead compound.

6. The method according to Claim 3, wherein (B) above is a combination of a lead compound and a copper compound.

7. The method according to Claim 3, wherein (C) above is a bromide.

8. The method according to Claim 3, wherein (C) above is a bromide quaternary ammonium salt.

9. The method according to any of Claims 1-8, wherein the aforementioned aromatic nitro compound is nitrobenzene.

10. The method according to any of Claims 1-9, wherein the aforementioned aromatic nitro compound is present in the reaction system in an amount in the range of 1-100 wt% with respect to the aromatic hydroxy compound.

11. The method according to any of Claims 1-10, wherein the aforementioned aromatic hydroxy compound is phenol.

Detailed explanation of the invention

[0001]

Industrial application field

The present invention concerns a method for manufacturing aromatic carbonic acid esters, and more specifically, the present invention concerns a method for the manufacture of aromatic carbonic acid esters which has excellent specificity and little production of impurities. Aromatic carbonic acid esters are compounds that are useful as raw materials for organic syntheses, and diphenyl carbonate in particular is receiving attention as a raw material for polycarbonate and other substances.

[0002]

Prior art

In the past, methods wherein an aromatic hydroxy compound and phosgene were allowed to react have been used as methods for manufacturing aromatic carbonic acid esters. However, a change in manufacturing methods is desired due to the high toxicity of phosgene. Thus, a method for the manufacture of aromatic carbonic acid ester from an aromatic hydroxy compound, carbon monoxide and oxygen has been offered as a method that does not use phosgene.

[0003]

With regard to catalysts that are used in such methods, a method is described in Japanese Kokoku Patent No. Sho 56[1981]-38144, wherein a palladium compound, a compound containing a metal from group IIIA, IVA, VA, VIA, IB, IIB, VIB or VIIB of the periodic table and a base are used; a method is described in Japanese Kokoku Patent No. Sho 56[1981]-38145, wherein a palladium compound, manganese complex, cobalt complex, base and desiccant are used; a method is described in Japanese Kokai Patent Application No. Hei 1[1989]-165551, wherein a palladium compound, iodine compound and zeolites are used; a method is described in Japanese Kokai Patent Application No. Hei 2[1990]-104564, wherein a palladium compound, divalent or trivalent manganese compound, tetraalkylammonium halide and quinones are used; a method is described in Japanese Kokai Patent Application No. Hei 2[1990]-142754, wherein a palladium compound, divalent or trivalent cobalt compound, tetraalkylammonium halide

and quinones are used; a method is described in Japanese Kokai Patent Application No. Hei 5[1993]-25095, wherein a palladium or palladium compound, cobalt compound, halide and basic compound are used; a method is described in Japanese Kokai Patent Application No. Hei 5[1993]-39247, wherein a palladium compound, copper compound, quinones and onium halide are used, a method is described in Japanese Kokai Patent Application No.

Hei 5[1993]-58961, wherein palladium or one or more types of palladium compound, a cobalt compound and alkali metal halide are used; a method is described in Japanese Kokai Patent Application No. Hei 5[1993]-97775, wherein a palladium compound, a quaternary ammonium salt, a metal auxiliary catalyst selected from among cobalt, iron, cerium, manganese, molybdenum, samarium, vanadium, chromium and copper, and an organic auxiliary catalyst selected from an aromatic ketone, aliphatic ketone and aromatic polycyclic hydrocarbon are used; a method is described in Japanese Kokai Patent Application No. Hei 6[1994]-9505, wherein a palladium compound, cerium compound and quaternary ammonium salt are used; a method is described in Japanese Kokai Patent Application No. Hei 6[1994]-41020 wherein a palladium compound, a metal auxiliary catalyst selected from manganese, cobalt and copper, and a nitrile compound are used; a method is described in Japanese Kokai Patent Application No. Hei 6[1994]-172268 wherein a palladium compound, 5-coordinated cobalt complex and quaternary onium salt are used; a method is described in Japanese Kokai Patent Application No. Hei 6[1994]-172269, wherein a palladium compound, an inorganic auxiliary catalyst selected from cobalt, manganese and copper, a quaternary onium salt and terpyridine or other organic cocatalyst are used; a method is described in Japanese Kokai Patent Application No. Hei 6[1994]-211750, wherein

a palladium compound, a monovalent or divalent copper compound and an ammonium halide compound are used; a method is described in Japanese Kokai Patent Application No. Hei 7[1995]-188116, wherein a catalyst is used which is produced by activating a precious metal catalyst in a carbon monoxide atmosphere; a method is described in Japanese Kokai Patent Application No. Hei 7[1995]-247243, wherein a reaction is carried out while evaporating off the water that is by-produced in the reaction; and a method is described in European Patent Application No. 0663388, wherein a palladium compound, lead compound and quaternary ammonium or quaternary phosphonium halide are used.

[0004]

Problems to be solved by the invention

However, although the methods that employ the various types of catalysts described above do increase the reactivity, the aromatic hydroxy compound is allowed to react in the presence of an oxidant, and it is thus impossible to avoid the production of poly(oxyarylene) by-products which are oxidative coupling products of the aromatic hydroxy compound. The selectivity of the aromatic carbonic acid ester based on an aromatic hydroxy compound standard is thus generally reduced. In addition, of these by-products, the dimers are extremely difficult to separate from the aromatic carboxylate esters by means of distillation or other methods. Thus, the objective of the present invention is to offer a method for efficiently manufacturing aromatic carbonic acid esters while reducing the amount of by-product oxidative coupling compounds.

[0005]

Means to solve the problems

The inventors of the present invention et al., as a result of painstaking investigations with the objectives described above, arrived at the present invention upon discovering that the selectivity of the target aromatic carbonic acid ester could be improved by means of carrying out the reaction in the presence of an aromatic nitro compound. Specifically, the present invention is a method for manufacturing aromatic carbonic acid esters wherein an aromatic hydroxy compound is allowed to react with oxygen and carbon monoxide, said method for manufacturing aromatic carbonic acid esters being characterized in that said reaction is carried out in the presence of aromatic nitro compound.

[0006]

Embodiment of the invention

1. Reaction raw materials

1) Aromatic hydroxy compound

The aromatic hydroxy compound that is used in the present invention can be any substance, provided that it is an aromatic mono- or polyhydroxy compound. Examples include phenol cresol, xylenol, trimethylphenol, tetramethylphenol, ethylphenol, propylphenol, methoxyphenol, ethoxyphenol, chlorophenol,

dichlorophenol, bromophenol, dibromophenol and other substituted phenols and isomers thereof; naphthol, methylnaphthol, ethylnaphthol, chloronaphthol, bromonaphthol and other substituted naphthols and isomers thereof; 2,2-bis(4-hydroxyphenyl)propane and various other types of bisphenols; various types of biphenols; various heteroaromatic hydroxy compounds and isomers thereof, and compounds formed by the substitution of alkyl groups or halogen atoms thereupon. Phenol is particularly desirable among these substances.

[0007]

2) Carbon monoxide

The carbon monoxide that is used in the present invention can be a gas that is produced by starting with a highly pure substance and diluting it with another gas that does not have a detrimental influence on the reaction, such as nitrogen, argon, carbon dioxide or hydrogen.

[0008]

3) Oxygen

The oxygen that is used in the present invention can be a gas that is produced by starting with a highly pure substance and diluting it with another gas that does not have a detrimental influence on the reaction, such as [atmospheric] air, nitrogen, argon, carbon dioxide or hydrogen.

[0009]

4) Aromatic nitro compound

The aromatic nitro compound that is used in the present invention is an aromatic mononitro or dinitro compound, examples of which include nitrobenzene, nitrotoluene, ethylnitrobenzene, dimethylnitrobenzene, methoxynitrobenzene, chloronitrobenzene, bromonitrobenzene, nitrophenol, dinitrobenzene, dinitrotoluene, dinitrophenol and other nitrobenzenes having substituents and isomers thereof, and nitronaphthalene, dinitronaphthalene and other nitronaphthalenes and isomers thereof. Of these substances, nitrobenzene and nitrotoluene (including their various isomers) are particularly desirable. The amount of aromatic nitro compound that is present in the reaction system is preferably a weight ratio of 1-200% with respect to the raw material aromatic hydroxy compound, with 1-100% being especially desirable. If the amount used is too small, the effects of the present invention will be slight, whereas if this amount is too large, the rate of production of diphenyl carbonate will be small. Aliphatic nitro compounds are undesirable because they impede the reaction.

[0010]

2. Catalyst

In the method of the present invention, it is desirable to use a catalyst, and particularly, a palladium system catalyst. Although conventional known catalysts can be used, a particularly desirable catalyst that can be cited is a palladium system

catalyst that consists of a combination of one or more types of substances selected from each of the components (A)-(C) below.

(A) Palladium or palladium compound

Examples of palladium or palladium compounds include palladium black, palladium carbon, palladium/alumina, palladium/silica or other carried palladiums; palladium chloride, palladium bromide, palladium iodide, palladium sulfate, palladium nitrate or other inorganic palladium salts; and palladium acetate, palladium oxalate or other organic palladium acid salts. In addition, substances that can also be used include palladium (II) acetylacetonate, palladium complexes produced by the coordination of carbon monoxide, nitriles, amines, phosphines or olefins on palladium, examples of which include $\text{PdCl}_2(\text{PhCN})_2$, $\text{PdCl}_2(\text{PPh}_3)_2$, $\text{Pd}(\text{CO})(\text{PPh}_3)_3$, $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$, $\text{Pd}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$, $[(\eta^3\text{-C}_3\text{H}_5)\text{PdCl}]_2$, $\text{Pd}(\text{DBA})_2$ and $\text{Pd}_2(\text{DBA})_3 \cdot \text{CHCl}_3$ (where Ph denotes a phenyl group, and DBA denotes dibenzylidene acetone) or mixtures of palladium and compounds that these complexes generate in the reaction system. Of these substances, palladium acetate and palladium/carbon are preferred. The amount of palladium component that is used in the present invention is preferably selected from a molar ratio in the range of 10^{-7} to 10^{-2} with respect to the aromatic hydroxy compound, with a range of 10^{-6} to 10^{-3} being particularly desirable.

[0011]

(B) Metal or metal compounds having a greater oxidation potential than palladium (reoxidant)

Any well-known metal or metal compound can be used as the reoxidant, provided that it is a metal or metal compound that has an oxidation potential that is higher than that of palladium. Specific desirable examples include manganese, cobalt, cerium, copper iron, lead and other metals, halides, organic acid salts, inorganic acid salts, oxides, alkoxides, aryloxides, and complexes thereof. These substances can be used individually, or a number of them can be used in combination. Of these substances, systems that contain lead compounds are particularly desirable, and it is additionally desirable to use a system comprising a combination of lead compound and copper compound. The amount of reoxidant that is used in the reaction has no particular restrictions, but it is preferable for the molar ratio to be in the range of 10^{-4} to 10^{-1} with respect to the aromatic hydroxy compound, with a range of 10^{-4} to 10^{-2} being preferred.

[0012]

(C) Halide compound

Any halogen salt can be used as the halide. Examples include quaternary ammonium halides, quaternary phosphonium halides, alkali metal halides, and alkaline-earth metal halides. Bromides are generally preferred, although this differs depending on such factors as the reaction conditions and the type of reoxidant that is used. Quaternary ammonium bromide salts are particularly desirable. There are no particular restrictions on the amount of halide that is used in the reaction, but it is preferable for the molar ratio to be in the range of 10^{-4} to 1 with respect to the

aromatic hydroxy compound, with a range of 10^{-3} to 10^{-1} being particularly desirable.

[0013]

3. Reaction conditions

The reaction is carried out by introducing the aforementioned aromatic hydroxy compound, aromatic nitro compound and palladium-system catalyst, preferably a catalyst composed of component (A), (B) and (C) above, into a reaction apparatus, pressurizing the system with carbon monoxide and oxygen, and then stirring the reaction well while heating. The absolute pressure during the reaction is a total pressure of 1-500 atm, with a range of 1-250 atm being preferred. Based on considerations pertaining to stability, the compositional ratio of the carbon monoxide and oxygen is preferably a ratio that is distant from the combustion range. The partial pressures of the carbon monoxide and oxygen are preferably 30-100 atm and 1-10 atm respectively, and the reaction temperature is in the range of 20-300°C, with 80-250°C being preferred. Although the reaction time will differ depending on the reaction conditions, the reaction time is ordinarily a few minutes to a few hours. During the reaction, hydroquinone and other such aromatic diols, quinones that are oxidation products thereof, and amines or other organic additives, which are used in conventional catalyst systems, can be added to the reaction system. In addition, examples of inert solvents that can be used include inert solvents such as hexane, heptane, cyclohexane, benzene, toluene,

xylene, methylene chloride, chloroform, chlorobenzene, ethyl ether, phenyl ether, tetrahydrofuran, dioxane and acetonitrile.

[0014]

Application examples

The present invention is described in detail below by providing application examples and comparative examples. Of the reaction products, the produced amounts of diphenyl carbonate, phenyl salicylate, p-phenoxyphenol, o-bromophenol and p-bromophenol were determined by gas chromatographic analysis (capillary column BP-X-5; 50→300°C, manufactured by SGE) with n-pentadecane as an internal standard, and the amount of carbon dioxide produced was determined by concentration analysis using a CO₂ detection tube manufactured by Gastech. The LC purity expresses the ratio of surface areas in the reaction liquid determined by liquid chromatographic analysis (column: Shodex OPD-50, manufactured by Showa Denko, liquid phase: acetonitrile/water, detection: UV 210 nm).

[0015]

Application Example 1

12.23 g (130 mmol) phenol, 1.23 g (10 mmol) nitrobenzene, 10.22 mg (4.8 μmol Pd) 5% palladium/carbon (N.E. Chemcat), 10.71 mg (48 μmol) lead (II) oxide, 3.82 mg (48 μmol) lead (II) oxide (I believe this is an error, 3.82 mg of PbO does not result in 48 μmol, besides already added PbO. I guess correct catalyst

is CuO - MW=79.5), and 154.1 mg (1.0 mmol) tetramethylammonium bromide were introduced into an autoclave with an inner volume of 50 mL. After replacing the interior of the system with carbon monoxide, carbon monoxide was introduced at 60 atm, dry air was introduced at 30 atm, and the reaction was mixed by stirring for 3 h at 100°C using an induction stirrer. After completion of the reaction, the liquid phase and gas phase were both subjected to quantitative analysis by gas chromatography. The results gave a diphenyl carbonate yield of 13.19% (8.56 mmol) with respect to phenol. Phenyl salicylate was produced as a by-product at 0.49% with respect to the diphenyl carbonate, p-phenoxyphenol was produced at 0.83% with respect to the diphenyl carbonate, bromophenol was produced at 27.8% with respect to the tetramethylammonium bromide that was used, and carbon dioxide was produced at 27.9% with respect to the carbonic acid ester. The LC purity was 85.0%.

[0016]

Comparative Example 1

A reaction was carried out in the same manner as in Application Example 1, with the exception that nitrobenzene was not used. The results produced a diphenyl carbonate yield of 12.47% (8.10 mmol) with respect to the phenol. In addition, phenyl salicylate was produced as by-product at 0.63% with respect to the diphenyl carbonate, p-phenoxyphenol was produced at 1.33% with respect to the carbonic acid ester, bromophenol was produced at 20.7% with respect to the tetramethylammonium bromide

that was used, and carbon dioxide was produced at 33.7% with respect to the carbonic acid ester. The LC purity was 83.9%.

[0017]

Comparative Example 2

A reaction was carried out in the same manner as in Application Example 1, with the exception that nitromethane was used instead of nitrophenol. The results indicated an amount of produced diphenyl carbonate of less than 0.1%.

[0018]

Application Examples 2-4

Reactions were carried out in the same manner as in Application Example 1, with the exception that the amounts of phenol and nitrobenzene were changed. The amounts of phenol and nitrobenzene, the amount of diphenyl carbonate produced, the yields of phenyl salicylate, p-phenoxyphenol and carbon dioxide with respect to the diphenyl carbonate, the yield of bromophenols with respect to the tetramethylammonium bromide that was used, and the LC purity are shown in Table I.

[0019]

Table I

PhOH: Phenol
PhNO₂: Nitrobenzene
DPC: Diphenyl carbonate
PS: Phenyl salicylate
p-POP: p-Phenoxyphenol
BP: Bromophenol (total of ortho- and para-isomers,
meta-isomer not measured)
ND: Not determined.

Key: 1 Application Example
 2 LC Purity

[0020]

Application Examples 5-7

Reactions were carried out in the same manner as in Application Example 1, with the exception that various types of aromatic nitro compounds were used instead of nitrobenzene. The amounts of produced aromatic nitro compound and diphenyl carbonate, the yields of phenyl salicylate, p-phenoxyphenol and carbon dioxide with respect to the diphenyl carbonate, and the yield of bromophenols with respect to the tetramethylammonium bromide that was used and the LC purity are shown in Table II.

[0021]

Table II

ArNO₂: Type of aromatic nitro compound

DPC: Diphenyl carbonate

PS: Phenyl salicylate

p-POP: p-Phenoxyphenol

BP: Bromophenol (total of ortho- and para-isomers,

meta-isomer not measured)

Key: 1 Application Example
 2 4-Nitrobenzene
 3 2-Nitrotoluene
 4 2-Nitro-m-xylene
 5 LC Purity

[0022]

Application Example 8

103.5 g (1.1 mol) phenol, 12.31 g (100 mmol) 38.31 mg (18 μ mol Pd) palladium/carbon (N.E. Chemcat), 80.35 mg (360 μ mol) lead (II) oxide, 28.63 mg (360 μ mol) copper (II) oxide and 1.11 g (7.2 mmol) tetramethylammonium bromide were introduced into a Hastelloy autoclave with an inner volume of 300 mL. After replacing the interior of the system with carbon monoxide/air = 2/1 mixed gas, this mixed gas was introduced at 90 atm. The reaction was mixed by stirring at 100°C while under a continuous flow of 0.6 L/min (ambient pressure conversion) of mixed gas. At 2 h after initiation of the reaction, some of the reaction liquid was sampled through a sintered filter, and was subjected to gas chromatographic and liquid chromatographic analyses. In addition, the concentration of carbon dioxide in the exhaust gas was analyzed at the same time. Similar analyses were carried out every 2 h thereafter, and the produced amount of diphenyl carbonate, the yields of phenyl salicylate, p-phenoxyphenol and carbon dioxide with respect to diphenyl carbonate, the yield of bromophenols with respect to the tetramethylammonium that was

used, and the LC purity for each time point are shown in Table III.

[0023]

Table III

DPC: Diphenyl carbonate

PS: Phenyl salicylate

p-POP: p-Phenoxyphenol

BP: Bromophenol (total of ortho- and para-isomers, meta-isomer not measured)

Key: 1 Time (h)
 2 LC Purity

[0024]

Application Example 9

A reaction was carried out in the same manner as in Application Example 8, with the exception that 69.0 g (733 mmol) phenol and 34.5 g (280 mmol) nitrobenzene were used. The amount of diphenyl carbonate produced during this reaction, the yields of phenyl salicylate, p-phenoxyphenol and carbon dioxide with respect to diphenyl carbonate, the yield of bromophenols with respect to the tetramethylammonium that was used, and the LC purity are shown in Table IV.

[0025]

Table IV

DPC: Diphenyl carbonate
PS: Phenyl salicylate
p-POP: p-Phenoxyphenol
BP: Bromophenol (total of ortho- and para-isomers,
meta-isomer not measured)
ND: Not determined.

Key: 1 Time (h)
2 LC Purity

[0026]

Comparative Example 3

A reaction was carried out in the same manner as in Application Example 8, with the exception that nitrobenzene was not used. The amount of diphenyl carbonate produced during this reaction, the yields of phenyl salicylate, p-phenoxyphenol and carbon dioxide with respect to diphenyl carbonate, the yield of bromophenols with respect to the tetramethylammonium that was used, and the LC purity are shown in Table V.

[0027]

Table V

DPC: Diphenyl carbonate

PS: Phenyl salicylate

p-POP: p-Phenoxyphenol

BP: Bromophenol (total of ortho- and para-isomers,
meta-isomer not measured)

Key: 1 Time (h)
 2 LC Purity

[0028]

Effect of the invention

As is clear from the examples described above, the production of oxidative by-products is controlled and the reaction efficiency based on an aromatic hydroxy compound is greatly improved by means of the present invention. The industrial merit of the method of the present invention is thus extremely high.

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